



## Effects of biochar on the emissions, soil distribution, and nematode control of 1,3-dichloropropene

Daniel J. Ashworth, Scott R. Yates & Guoqing Shen

To cite this article: Daniel J. Ashworth, Scott R. Yates & Guoqing Shen (2017) Effects of biochar on the emissions, soil distribution, and nematode control of 1,3-dichloropropene, Journal of Environmental Science and Health, Part B, 52:2, 99-106, DOI: [10.1080/03601234.2016.1239981](https://doi.org/10.1080/03601234.2016.1239981)

To link to this article: <http://dx.doi.org/10.1080/03601234.2016.1239981>



Published online: 24 Oct 2016.



Submit your article to this journal [↗](#)



Article views: 56



View related articles [↗](#)



View Crossmark data [↗](#)

## Effects of biochar on the emissions, soil distribution, and nematode control of 1,3-dichloropropene

Daniel J. Ashworth<sup>a</sup>, Scott R. Yates<sup>b</sup>, and Guoqing Shen<sup>c</sup>

<sup>a</sup>Department of Environmental Sciences, University of California, Riverside, California, USA; <sup>b</sup>USDA-ARS, Salinity Laboratory, Riverside, California, USA;

<sup>c</sup>School of Agriculture and Biology, Shanghai Jiao Tong University, Shanghai, P.R. China

### ABSTRACT

Emissions of volatile soil fumigant 1,3-dichloropropene (1,3-D) from soil to air are a significant concern in relation to air quality, and cost-effective strategies to reduce such emissions are urgently required by growers to help them comply with increasingly stringent regulations. In this work, application of a rice husk-derived biochar to the surface of a sandy loam soil chamber reduced soil–air emissions of 1,3-D from 42% in a control (no biochar) to 8% due to adsorption onto the biochar. This adsorbed 1,3-D showed a potential for re-volatilization into air and solubilization into the soil–liquid phase. Biochar at the soil surface also reduced soil–gas concentrations in the upper soil; based on the determination of concentration–time values, this may limit 1,3-D-induced nematode control in the upper soil. In batch studies, the mixing of biochar into the soil severely limited nematode control; 1,3-D application rates around four times greater than the maximum permissible limit would be required to give nematode control under such conditions. Therefore, the use of biochar as a surface amendment, while showing an emission reduction benefit, may limit pest control during subsequent fumigations if, as seems probable, it is plowed into the soil.

### ARTICLE HISTORY

Received 14 June 2016

Accepted 22 August 2016

### KEYWORDS

Fumigant emission reduction; 1,3-D; efficacy; concentration time index; adsorption

### Introduction

Biochar, the carbon-rich material obtained by heating biomass, such as wood, manure, or leaves, under a limited oxygen supply (i.e. the process of pyrolysis), is receiving significant attention as a soil amendment that (i) improves soil properties,<sup>[1–3]</sup> (ii) provides an avenue for waste disposal/management, (iii) allows for the co-production of bio-energy sources,<sup>[4]</sup> and (iv) assists in the fight against climate change.<sup>[5,6]</sup> Current interest in biochar relates primarily to its potential for climate change abatement; specifically in relation to C cycling. Plants assimilate CO<sub>2</sub> from the atmosphere and convert it to biomass C via photosynthesis; upon decomposition of the plant material, this C is released back to the atmosphere as CO<sub>2</sub>, a greenhouse gas. However, converting this biomass into biochar, which decomposes much more slowly, diverts C from the rapid biological cycle into a much slower biochar cycle.<sup>[5]</sup> Since biochar C half-lives range from 10<sup>2</sup> to 10<sup>7</sup> years,<sup>[7]</sup> CO<sub>2</sub> emissions can be mitigated.

Given the significant potential benefits of applying biochar to soils, it is likely that its use will increase in the future. On this basis, it is useful to determine the extent to which biochar can mitigate environmental pollution for a range of soil contaminants. Biochar can adsorb a wide range of organic chemical and heavy metal contaminants in soils and prevent their transport within the environment.<sup>[8,9]</sup> The retention of organic contaminants is likely due to its highly porous nature, large surface area, and preponderance of chemical functional groups. Indeed, Kookana<sup>[10]</sup> reported that the pesticide adsorption potential of

biochar is more than 2,000 times greater than that of soil. However, little work has addressed the use of biochar in reducing soil–air emissions of volatile agricultural fumigants.

1,3-dichloropropene (1,3-D) is a broad spectrum soil fumigant with a range of biocidal properties.<sup>[11]</sup> Its use in areas such as California is common due to the prevalence of high-cash crops requiring a high degree of pest suppression, particularly the control of nematodes. Indeed, 1,3-D was ranked the most used fumigant (based on mass applied) in California in 2012; in the same year, it was ranked the third most used pesticide (based on mass applied).<sup>[12]</sup> However, its high vapor pressure and Henry's constant ensure that a high proportion of its applied soil mass transfers to the atmosphere unless abatement strategies are employed. As a volatile organic compound, its toxic nature and role in the formation of near-surface ozone (photochemical smog) are significant in terms of air quality. Therefore, the use of 1,3-D is strictly controlled in California. Alternative approaches for reducing the soil–air emissions of 1,3-D are highly desirable, especially if they are cost-effective and provide additional advantages to growers and regulators; biochar may meet these criteria.

The application of biochar to a soil surface has been shown to be highly effective at reducing the emissions of 1,3-D relative to a bare soil, with reductions of greater than 92%.<sup>[13,14]</sup> A similar level of emission reduction has also been shown for the soil fumigant chloropicrin.<sup>[15]</sup> However, little other information is available. Therefore, we aimed to obtain additional data on the effects of biochar on 1,3-D emissions. The novel aspect of the

work was in addressing further the following important questions related to the surface application of biochar to fumigated soils: (i) Does biochar application to the soil surface affect 1,3-D soil–gas distribution, and hence pest control potential? (ii) What is the fate (degradation, re-volatilization, and leachability potential) of biochar-adsorbed 1,3-D? (iii) What effect does the subsequent plowing of biochar into the soil have on the future fumigation efficacy?

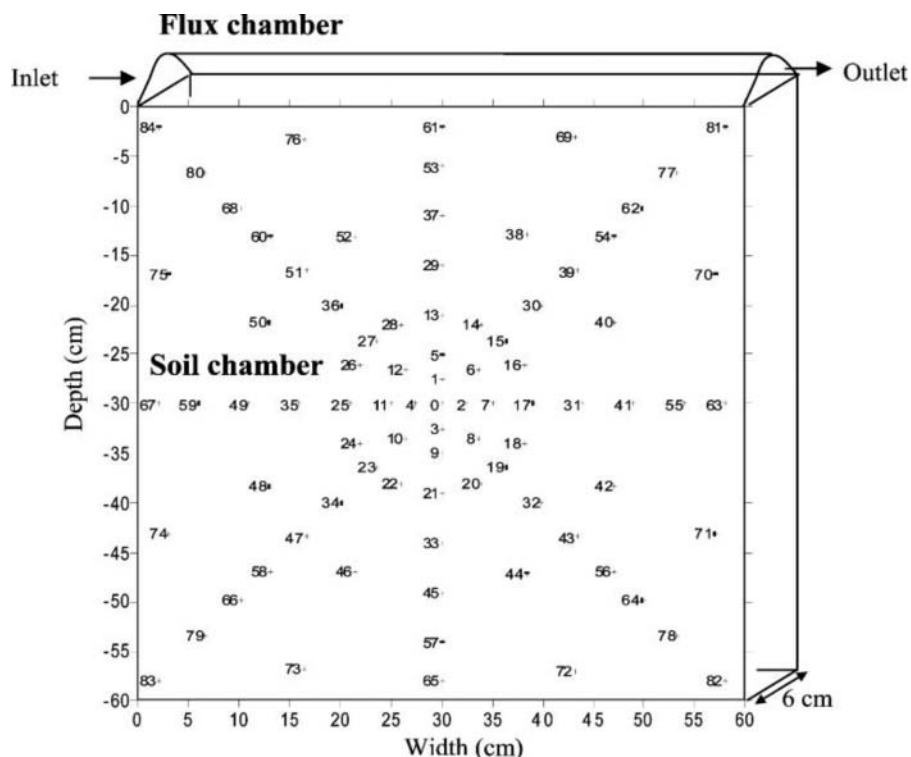
## Materials and methods

### 2-D soil chamber

A leakproof stainless steel soil chamber was used to determine the two-dimensional (2D) soil distribution and soil–air emissions of 1,3-D in the presence and absence (control) of surface-applied biochar. The 2D chamber has been described previously.<sup>[16,17]</sup> It was constructed from 0.5-cm stainless steel and was 60 cm wide, 60 cm tall, and 6 cm thick (Fig. 1). On the face of the chamber, 84 sealable sampling ports extended radially from a central injection port so that soil–gas concentrations could be measured in real time. The soil used was an Arlington sandy loam (75% sand, 18% silt, 7% clay, and 0.92% organic matter, pH 7.2) collected from the upper 20 cm of Field 2B of the University of California – Riverside Experimental Station. As used, the gravimetric moisture content of the soil was 5%. For the control, the chamber was filled with soil in 5-cm depth intervals to a uniform bulk density (dry equivalent) of 1.5 g cm<sup>-3</sup>. For the biochar-amended treatment, a biochar was prepared from dried, ground (<3 mm) rice husks that were placed into lidded crucibles and pyrolyzed at 400°C for 5 h.

A biochar/water slurry (1:1.5 w/w) was prepared for use in the chamber. The use of a slurry is preferred over dry biochar for surface applications because under field conditions wind loss is less of an issue. The chamber was packed in the same way as the control except that in the uppermost layer only 4 cm of soil was used; the remaining 1 cm was applied with 270 g of biochar slurry. This surface application was equivalent to a 1% dry biochar addition to the top 20 cm of soil, which is a commonly used rate in experiments studying biochar effects on fumigant behavior.<sup>[13–15,18,19]</sup> To the top of the chamber was then sealed a galvanized sheet metal dynamic flux chamber with a sampling section of 60×6 cm and an air inlet at one end and outlet at the other end (Fig. 1). The flux chamber was dome-shaped to minimize the dead space (i.e. zero or low velocity zones) when drawing air across the soil surface to measure emissions.

At time 0, 567 mg of 1,3-D donated by Dow Agrosciences (Indianapolis, IN, USA) was injected into the soil via Port 0 at the center of the chamber (this equates to an application rate of approximately 157 kg ha<sup>-1</sup>; an intermediate rate based on the chemical's label recommendations). Immediately, air was drawn across the soil surface at a flow rate of 430 mL min<sup>-1</sup>; this ensured no significant pressure deficit within the chamber with respect to the ambient pressure.<sup>[17,20]</sup> At the inlet, a charcoal sorbent tube was fitted to clean the incoming ambient air. At the outlet, the air was directed via Teflon tubing through two Anasorb CSC charcoal sorbent tubes from SKC Inc (Eighty Four, PA, USA) connected in series (primary and backup tubes) to trap emitted 1,3-D. Each pair of tubes was sampled for 4 h. At 96 h, the sampling time was extended to 6 h, and at 222 h, it was extended to 12 h; this was done to ensure sufficient 1,3-D on charcoal tubes as emissions decreased. After sampling,



**Figure 1.** Schematic of the 2D experimental system consisting of a square soil chamber, a surface-mounted flux chamber, and numerous sampling ports surrounding the central injection port (marked 0). Biochar was applied to the soil surface.<sup>[17]</sup> © American Chemical Society. Reproduced by permission of American Chemical Society. Permission to reuse must be obtained from the rightsholder.

tubes were placed in a freezer at  $-19^{\circ}\text{C}$ . Emissions from the soil chamber were collected in this way for 366 h. At 2 h and 6 h, and on days 1, 2, 3, 4, 6, 8, 10, and 14, soil–gas samples (100  $\mu\text{L}$ ) were collected from the ports using a gas tight syringe and injected into 12-mL glass headspace vials, which were immediately sealed with a Teflon-faced septa and aluminum crimp cap.

On days 2, 4, 6, 8, 10, 12, and 14, the biochar on the soil surface was sampled by carefully opening the flux chamber and quickly removing three pairs of subsamples (approximately 0.5 g each) of biochar. The removed biochar was replaced with clean biochar before the flux chamber was resealed onto the soil chamber. The total amount of time for which the chamber was opened on each occasion was less than 2 min. Care was taken to avoid sampling the same location more than once. After weighing, one subsample from each pair was used to determine moisture content and the other was used for determination of 1,3-D content.

#### **Fate of biochar-adsorbed 1,3-D (batch incubation experiments)**

At the end of the experiment, the biochar was carefully removed from the soil surface and homogenized. The moisture content was determined and subsamples (0.6 g) were taken to determine any subsequent degradation, re-volatilization, and water extractability (as a proxy for leachability) of the adsorbed 1,3-D over time. These were placed into 20-mL glass vials, sealed with a Teflon-faced septa and aluminum crimp cap, and placed at either 25 or  $50^{\circ}\text{C}$ . At 0, 2, 5, 9, and 14 days, three vials were moved to a freezer at  $-19^{\circ}\text{C}$  for 24 h before acetone extraction and determination of total 1,3-D content (analysis is described below). At 14 days, an additional three incubated vials were used to quantify the potential for re-volatilization of 1,3-D from the biochar by the removal of 500  $\mu\text{L}$  of headspace gas using a needle injected through the septa. This gas sample was treated in the same manner as the gas samples from the chamber. Also, at 14 days, a further three vials were placed in a freezer at  $-19^{\circ}\text{C}$  for 24 h before water extraction and determination of potentially leachable 1,3-D content (see below).

#### **Nematode control (batch incubation experiments)**

Coupled batch experiments were used to determine nematode control by 1,3-D in the presence and absence of biochar. To 20-g samples of soil in a 150-mL glass bottle, 0.2 g of clean biochar (1% addition) was added and thoroughly mixed. Twenty-gram soil samples without biochar were used as controls. To each vial, 0.7 mL of an aqueous solution was added containing approximately 200 citrus nematode (*Tylenchulus semipenetrans*) individuals. The nematodes had been extracted from freshly collected citrus roots using the Baermann funnel technique.<sup>[21]</sup> The bottles were sealed and allowed to sit overnight before thorough mixing. A gradient of 1,3-D soil concentrations achieved by adding various amounts of 1,3-D (in 5- $\mu\text{L}$  aqueous solution) to the bottles, i.e. 0 (control), 0.32, 0.64, 1.59, 3.18, 6.35, 12.71, 25.41, 50.82, and 101.64  $\mu\text{g g}^{-1}$ . Immediately after dosing, each bottle was sealed with a septa and

aluminum cap. Five replicates were established for each concentration treatment. The bottles were then placed at  $25^{\circ}\text{C}$  for 48 h. After this time, the soil was removed from the bottles and the surviving nematodes were extracted using the Baermann funnel method. Following extraction, the aqueous solution containing live nematodes was quantitatively transferred to a Petri dish, and the number of nematodes was counted under a microscope. Nematode mortality was determined as follows:

$$\text{Mortality} = \left( 1 - \frac{\text{survival}_{\text{treated}}}{\text{survival}_{\text{control}}} \right) \times 100\%, \quad (1)$$

where  $\text{survival}_{\text{treated}}$  is the number of surviving nematodes in a 1,3-D treatment, and  $\text{survival}_{\text{control}}$  is the number of surviving in the control (i.e. without 1,3-D). To quantify nematode exposure to 1,3-D, the concentration–time index (CT), the integral of concentration over time is defined as follows:

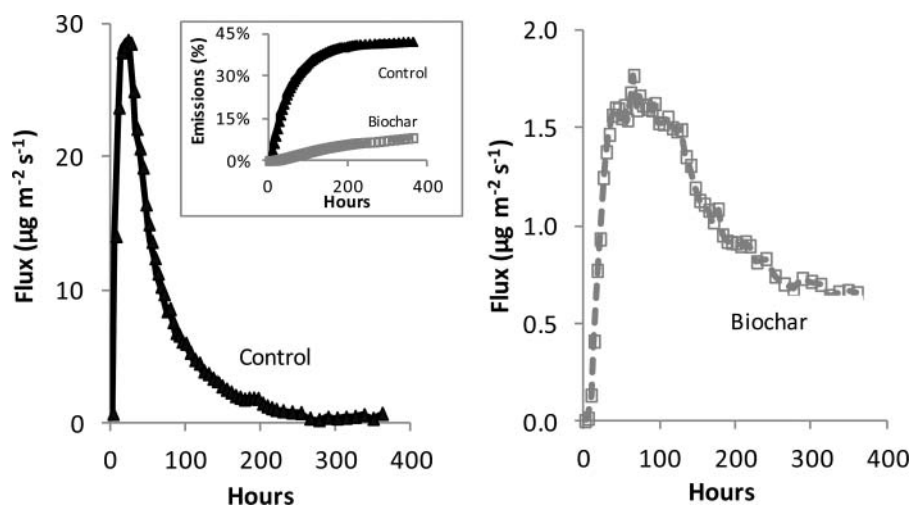
$$\text{CT}(t) = \int_0^t C(t)dt, \quad (2)$$

where  $C$  is the total 1,3-D concentration ( $\mu\text{g mL}^{-1}$ ), and  $t$  is the time (h).

#### **Extractions and analysis**

Charcoal tubes were extracted by removing the charcoal into a 12-mL glass vial, adding 4 mL of acetone (Fisher Scientific, Fair Lawn, NJ, USA), sealing with a Teflon-faced septa and aluminum crimp cap, and shaking for 1 h. Then, 1.5 mL of supernatant solvent was removed for analysis. The extraction efficiency of this procedure for 1,3-D was 86%, determined in preliminary experiments. The biochar subsamples were extracted in the same way but using 10 mL of acetone; the extraction efficiency of the procedure for the 1,3-D isomers was determined as 84%.<sup>[14]</sup> The water-extractable fraction of 1,3-D on the biochar was determined by adding 10 mL of deionized water, sealing as above, and shaking for 1 h. A 6-mL aliquot was then added to 2 mL of hexane (Fisher Scientific) in a glass vial, which was sealed as above and shaken for 30 min. Finally, a 1.5-mL subsample of hexane supernatant was removed by glass pipette into an amber GC vial. The final concentration was corrected for the efficiency of water extraction, which was 45%, determined in preliminary experiments.

Analysis of sorbent tube and biochar extracts was carried out using an Agilent 7890A gas chromatograph (GC), equipped with a micro-electron capture detector (Agilent Technologies, Wilmington, DE, USA). Analytical conditions were as described by Ashworth et al.<sup>[22]</sup> Soil–gas samples were analyzed using an Agilent 6890 GC equipped with a micro-electron capture detector and an Agilent G1888 automated headspace sampler. Analytical conditions were as described by Ashworth and Yates.<sup>[23]</sup> Appropriate blanks and standards were employed.



**Figure 2.** Emission fluxes of 1,3-D for the control (left) and biochar-amended (right) soil chambers (note the difference in y-axis scales). Inset shows total cumulative emissions of 1,3-D for both chambers.

## Results and discussion

### 2D soil chamber: emissions of 1,3-D

Cumulative total emissions and emission fluxes of 1,3-D over the 14 days of the experiment are shown in Figure 2 for the control (bare soil) and biochar-amended soil. In the control, 42.0% of the added 1,3-D was emitted from the soil. This value is consistent with previously reported 1,3-D emission levels in both field and laboratory studies.<sup>[24]</sup> Since the two dominant processes within the sealed chamber system are assumed to be emissions and degradation, the results suggest that approximately 60% of the added 1,3-D was degraded within the soil. The timing and the magnitude of the peak fumigant emission flux are important in relation to the human health risks associated with fumigant application. For the control chamber, the flux of 1,3-D showed a rapid increase after application, peaking at approximately  $29 \mu\text{g m}^{-2} \text{s}^{-1}$  at 24 h. After this time, fluxes decreased steadily with extensive tailing. Such behavior is typical for a bare soil.<sup>[22,25]</sup> In contrast, the biochar-amended soil showed a relatively slow increase in emission flux after application, with a maximum flux of approximately  $1.8 \mu\text{g m}^{-2} \text{s}^{-1}$  at 68 h. In addition to exhibiting much lower fluxes than the control, the biochar-amended flux curve was much broader, with a much less obvious emission peak. Lower fluxes resulted in the emission of approximately 8.0% of the 1,3-D added to the chamber. This value was approximately five times lower than that in the control, indicating that the biochar markedly reduced emissions.

### 2D soil chamber: soil-gas distribution of 1,3-D

Following the application in both cases, the 1,3-D gas extended radially from the central application point and tended toward a uniform distribution throughout the chamber (data not shown). Moreover, in both cases, dissipation of 1,3-D was more rapid in the upper half of the chamber than in the lower half due to surface volatilization. Close to the soil surface, the biochar-amended soil showed reduced soil-gas 1,3-D concentrations relative to the control. In

considering the eight gas sampling ports in the uppermost 8 cm of soil, a trend of lower 1,3-D soil-gas concentrations is seen in the biochar-amended soil (compared to the control) at all sampling times (apart from at 2 h when the gas had not yet reached the surface). For example, at 6 h (when the highest concentrations were observed), the biochar-amended soil showed lower 1,3-D concentrations (by 14 to 70%) than the control at each of the eight sampling ports. In the biochar-amended chamber the soil-gas concentrations for these ports averaged  $0.92 \mu\text{g mL}^{-1}$  compared with  $1.55 \mu\text{g h mL}^{-1}$  for the control chamber; this difference was statistically significant (paired t-test  $P < 0.05$ ). This suggests that adsorption of 1,3-D onto the biochar significantly reduced soil-gas concentrations in the upper soil; the effect of this process on the potential of pest control is considered below.

### 2D soil chamber: adsorption of 1,3-D onto biochar

At the end of the chamber experiment, the mass of 1,3-D adsorbed onto the biochar accounted for 32.5% of the 1,3-D applied. This level of adsorption accounts rather well for the difference in emissions between the control and the biochar-amended chambers (assuming some level of error in the measurements), indicating that 1,3-D adsorption onto the biochar was most likely responsible for the marked emission reductions observed. Other workers have observed dramatic reductions in 1,3-D emissions in biochar-amended soils. Shen et al.<sup>[14]</sup> used the same soil and rice husk biochar in 1D,  $150 \times 12$ -cm cylindrical columns and found that total 1,3-D emissions were reduced from 34.7% in the control (bare soil) to 0.27% in soil with a 1% biochar amendment to the surface. Using a biochar derived from green waste applied at the same rate, these workers found 1,3-D emissions of 1.7%. Using a biochar derived from wood, Wang et al.<sup>[13]</sup> found 1,3-D emissions ranging from  $<0.1$  to 2.9% for application rates ranging from 0.5 to 2% (compared with the emissions of 36 to 40% for a non-amended control). These dramatic reductions in emissions have been attributed to the adsorption of 1,3-D onto the biochar. Overall, research



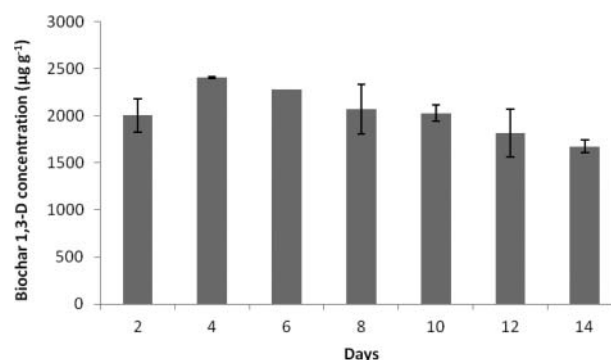
results thus far, including those from the present study, demonstrate that biochar has a large potential to adsorb 1,3-D and effectively limit its emission from soil to air.

In general, the microstructure of a biochar comprises closely packed and highly distorted aromatic ring layers,<sup>[6]</sup> and it has a turbostatic structure.<sup>[26]</sup> Surface functional groups such as carboxyl, phenolic, hydroxyl, etc, provide biochar with strong adsorption properties. Kolodynska et al.<sup>[27]</sup> also reported that the sorption capacity of a biochar depends mainly on its polarity, aromaticity, surface area, and pore size distribution. Analysis of the physicochemical properties of the rice biochar that we used<sup>[14]</sup> revealed the presence of an irregular mesopore structure, a specific surface area of  $6.18 \text{ m}^2 \text{ g}^{-1}$ , a dominance of Si minerals, a pH of 10.56, and a variety of oxygen- and hydrogen-containing functional groups. It is considered that these properties likely promoted the adsorption of 1,3-D onto the biochar and the observed reduction in emissions compared to the control.

#### **Fate of biochar-adsorbed 1,3-D (batch incubation experiments)**

Electron donors on biochar may catalyze the reduction of nitroaromatic compounds, such as 1,3-D, and enhance their degradation.<sup>[28]</sup> In the work by Shen et al.,<sup>[14]</sup> the data strongly suggested that the soil fumigant chloropicrin was degraded after adsorption onto biochar. The same workers therefore suggested that 1,3-D may also be degraded by biochar (although there was no evidence to support this hypothesis). In the present work, we tested this hypothesis by incubating the 1,3-D-laden biochar taken from the top of the chamber at the end of the experiment and determining the remaining 1,3-D concentrations over time. With incubation at  $25^\circ\text{C}$ , 1,3-D concentration on the biochar decreased by just 3.5% over two weeks, indicating negligible degradation. Therefore, we consider that significant degradation of adsorbed 1,3-D did not occur during our chamber experiment (also conducted at  $25^\circ\text{C}$ ). However, at  $50^\circ\text{C}$ , marked degradation occurred, with a decrease of 40.1% over two weeks. This suggests that under field conditions, where typical environmental conditions during soil fumigation treatment are likely to yield high ( $>40^\circ\text{C}$ ) temperatures in near-surface soil,<sup>[29]</sup> significant degradation of biochar-adsorbed 1,3-D may occur. This loss would limit the amount of 1,3-D in the biochar-adsorbed pool that would be available for subsequent potential transport via leaching and re-volatilization; thus, potentially limiting the future impact of 1,3-D on water and air quality (see below).

During our study, the amount of 1,3-D adsorbed on the biochar increased from  $2,004 \mu\text{g g}^{-1}$  on day 2 to a maximum of  $2,405 \mu\text{g g}^{-1}$  on day 4 before decreasing slowly over time (Fig. 3). These values indicate that adsorption occurred rapidly. Gradual decrease in the amount of 1,3-D adsorbed on the biochar after day 4 may imply that 1,3-D was re-volatilized from the biochar and emitted to air. An alternative explanation for the loss over time would be degradation, but this process can be discounted at  $25^\circ\text{C}$  temperature of the chamber (based on the degradation data discussed above). Indeed, re-volatilization seems to be a probable explanation because the soil–gas data (discussed above) indicate that extremely low amounts of 1,3-D



**Figure 3.** Average concentration of 1,3-D adsorbed on biochar at the surface of the soil chamber throughout the experiment. Error bars show  $\text{SD} = 1$ .

remained in the soil after day 4 and yet, compared to the control, emissions of 1,3-D persisted over an extended period in the biochar-amended column (Fig. 2). Our coupled batch study verified that re-volatilization may occur from the biochar. Although not designed to determine actual fluxes of 1,3-D (due to this being a closed system), the experiment indicated that even in the absence of an air flow across the soil surface, losses of 1,3-D at  $25^\circ\text{C}$  and  $50^\circ\text{C}$  were 0.015% and 0.028%, respectively, of the total within the system after 14 days. The higher value at  $50^\circ\text{C}$  was probably due to an increase in vapor pressure at higher temperature. This finding lends support to the hypothesis that the biochar within the chamber initially adsorbed 1,3-D and then slowly released it into air over time. To the best of our knowledge, this important environmental process has not been observed in previous fumigant/biochar studies.

In general, 1,3-D has been shown to be poorly retained in soils; indeed, Park et al.<sup>[30]</sup> reported low  $K_D$  and  $K_{OC}$  values for 1,3-D in the Arlington soil used in the present study.  $K_D$  is soil-water partition coefficient;  $K_{OC}$  is soil organic carbon-water partition coefficient. Its movement is considered to mainly occur in the gas phase rather than in the liquid phase due to its high Henry's law constant. However, surface-applied biochar containing a large amount of adsorbed 1,3-D may be subjected to differing physical processes that could result in the release of 1,3-D to the liquid phase during irrigation or rainfall. In our coupled batch study to quantify the potential for 1,3-D release from the biochar, the release of 1,3-D into the water at  $25^\circ\text{C}$  and  $50^\circ\text{C}$  was 0.078% and 0.064% of the total present in the system, respectively, after 14 days. In spite of relatively low levels of release, the data do indicate a potential for 1,3-D migration in the soil–liquid phase under field conditions. To date, 1,3-D has not been detected in groundwater and so is not considered a cause for concern.<sup>[31]</sup> However, groundwater monitoring studies have probably not included the potential influence of biochar-amended soils, where the biochar-adsorbed 1,3-D could act as a pool from which release may occur over time. This may require future research under field conditions.

#### **Nematode control (batch incubation experiments)**

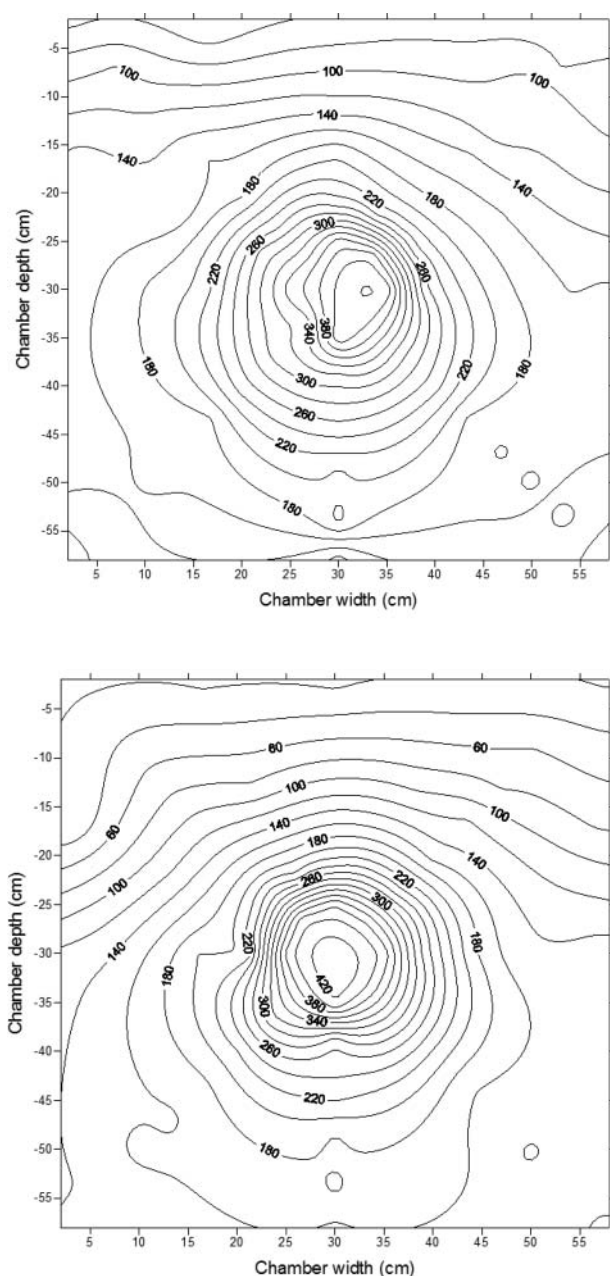
In the coupled batch experiments for determining nematode mortality at varying 1,3-D soil concentrations over 48 h, the results showed that a CT index between  $10 \mu\text{g h mL}^{-1}$  and  $25 \mu\text{g h mL}^{-1}$  was required to achieve 100% nematode kill ( $10 \mu\text{g}$

$\text{h mL}^{-1}$  gave a nematode mortality of 47%, and  $25 \mu\text{g h mL}^{-1}$  gave a mortality of 100%; data not shown). This range is broadly consistent with the value of  $12 \mu\text{g h mL}^{-1}$  reported previously [32,33] for citrus nematodes. Since  $25 \mu\text{g h mL}^{-1}$  was the lowest CT value in our study to yield 100% mortality, we used this value for subsequent comparison with the values of the chamber. Using the measured soil-gas concentrations in the soil chamber, we used Equation 2 to calculate CT values throughout the chamber at 48 h (i.e. the same time as the batch experiments) and compared these with the  $25\text{-}\mu\text{g h mL}^{-1}$  value required for mortality (Fig. 4). In the control chamber, values more than  $25 \mu\text{g h mL}^{-1}$  were observed throughout the chamber (range of 46 to  $415 \mu\text{g h mL}^{-1}$ ; average  $198 \mu\text{g h mL}^{-1}$ ). Even at the soil surface, where soil-gas concentrations were

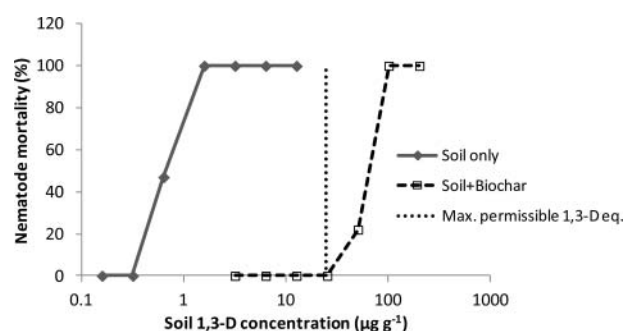
slightly depleted due to emission losses, CT values that would be effective at killing nematodes ( $>25 \mu\text{g h mL}^{-1}$ ) were observed. In the biochar-amended soil, CT values were in the range 15 to  $419 \mu\text{g h mL}^{-1}$  (average  $177 \mu\text{g h mL}^{-1}$ ) and declined more rapidly toward the surface than in the control chamber. In the majority of the chamber, the CT values were high enough to effect nematode kill ( $>25 \mu\text{g h mL}^{-1}$ ). However, the loss of gas phase 1,3-D at the soil surface (due to adsorption onto the biochar) yielded low CT values in this region of the biochar-amended chamber; in the top 2.5 cm, the average CT index at 48 h was just  $19 \mu\text{g h mL}^{-1}$ , and in the top 8 cm, it was  $27 \mu\text{g h mL}^{-1}$ . These values suggest that in soil with biochar amendment at its surface, complete pest kill via 1,3-D exposure may not be achieved close the soil surface. Under field conditions, this may have serious consequences for plant growth and yield; although this would likely be offset by high temperatures near the soil surface, aiding in nematode control. [29,33]

Graber et al. [19] reported that nematode mortality with 1,3-D was not adversely affected by biochar addition to soil. In contrast, in our coupled batch experiment comparing control and biochar-amended soil in terms of nematode kill, we found that much greater concentrations of 1,3-D were required to achieve 100% nematode mortality in the presence of biochar (Fig. 5). In the absence of biochar, an initial soil concentration of  $1.59 \mu\text{g g}^{-1}$  was sufficient to produce 100% mortality; whereas in the presence of biochar, an initial concentration  $\sim 60$  times greater ( $101.64 \mu\text{g g}^{-1}$ ) was required. It is important to remember here that the batch study used biochar mixed into the soil; therefore, it does not simulate a scenario where biochar is applied to the soil surface for emission reduction purposes. Rather, the batch study can be considered to simulate the mixing of biochar into the soil after emission reduction has been accomplished. For example, if biochar is used as an emission reduction strategy by application to the surface, it would likely be plowed into the soil prior to the next growing season. By plowing biochar into the soil rather than removing it, the soil and environmental benefits it offers can be attained. In any case, its removal from the soil surface and disposal would be difficult, time-consuming, and expensive.

The batch study clearly suggests that biochar plowed into the soil would likely seriously compromise nematode control during



**Figure 4.** Concentration time (CT) values ( $\mu\text{g h mL}^{-1}$ ) throughout the control (upper) and biochar-amended (lower) chambers at 48 h. Based on coupled batch experiments,  $\text{CT} > 25 \mu\text{g h mL}^{-1}$  was required for nematode control.



**Figure 5.** Nematode mortality against soil concentration in the presence and absence of biochar (mixed into soil) after 48-h exposure. Note log scale on  $x$ -axis. Vertical dotted line shows equivalent soil concentration ( $24.8 \mu\text{g g}^{-1}$ ) for the California maximum permissible field application rate of  $372 \text{ kg ha}^{-1}$  (assuming that 1,3-D diffuses through the upper 1 m of soil with a bulk density of  $1.5 \text{ g cm}^{-3}$ ).

subsequent fumigations. The extensive contact between the biochar and the applied 1,3-D within the soil results in a significant degree of adsorption; thus, at typical application rates, insufficient “free” 1,3-D would persist to effect nematode kill. Overall, these results suggest that although biochar does not significantly compromise nematode control when applied to the surface (except for in the upper soil layer), its subsequent plowing into the soil would likely render future fumigations ineffective unless very high application rates are used. For example, in our batch study, the initial soil concentrations required for 100% nematode control in the absence ( $1.59 \mu\text{g g}^{-1}$ ) and presence ( $101.64 \mu\text{g g}^{-1}$ ) of biochar relate to equivalent field application rates of 24 and  $1524 \text{ kg ha}^{-1}$ , respectively (assuming that in the field, 1,3-D diffuses throughout the upper 1-m of soil having a bulk density of  $1.5 \text{ g cm}^{-3}$ ). In California, the maximum permissible broadcast application rate for 1,3-D is  $372 \text{ kg ha}^{-1}$ ,<sup>[34]</sup> therefore, our data suggest that when biochar is mixed into the soil at an equivalent rate of 1%, a 1,3-D application rate around four times greater than the maximum permissible rate would be required to produce effective nematode control.

## Conclusions

In concurrence with other studies, soil surface application of biochar is shown to be an effective approach for mitigating 1,3-D emissions due to rapid and high adsorption of the chemical. A novel component of this study was in quantifying the effect of this adsorption on nematode control. With surface biochar application, nematode control via 1,3-D exposure is potentially reduced near the soil surface due to the depletion of soil-gas 1,3-D concentrations via adsorption onto the biochar. Nevertheless, at greater depths, nematode control is likely unaffected in this scenario. Significantly, however, mixing/plowing of the biochar into the soil (e.g. after emission reduction has been achieved) to obtain its soil/environmental benefits would likely severely limit the nematode control of future fumigations due to a high level of 1,3-D adsorption throughout the plow layer. The adsorption of 1,3-D onto biochar may result in a pool of fumigant that is available for future re-volatilization and leaching; the potential for both such processes was observed in our study and represents a further novel aspect of the work. Therefore, the agricultural and environmental consequences of biochar application for fumigant emission reduction should be carefully considered. For example, perhaps biochars with differing fumigant adsorption properties, or application rates lower than the 1% rate used in this study, may be better able to mitigate emissions and still allow for adequate pest control; this requires additional research.

## Acknowledgments

The authors thank Qiaoping Zhang for technical assistance throughout the study. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products. The use of trade, firm, or corporation names in this document is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the United States Department of Agriculture or the Agricultural Research Service of any product or service to the exclusion of others that may be suitable.

## References

- [1] Lehmann, J.; Rillig, M.C.; Thies, J.; Masiello, C.A.; Hockaday, W.C.; Crowley, D. Biochar effects on soil biota – a review. *Soil Biol. Biochem.* **2011**, *43*, 1812–1836.
- [2] Alburquerque, J.A.; Salazar, P.; Barron, V.; Torrent, J.; del Campillo, M.D.; Gallardo, A.; Villar, R. Enhanced wheat yield by biochar addition under different mineral fertilization levels. *Agron. Sustain. Dev.* **2013**, *33*, 3475–3484.
- [3] Schmidt, H.P.; Kammann, C.; Niggli, C.; Evangelou, M.W.H.; Mackie, K.A.; Abiven, S. Biochar and biochar-compost as soil amendments to a vineyard soil: Influences on plant growth, nutrient uptake, plant health and grape quality. *Agric. Ecosyst. Environ.* **2014**, *191*, 117–123.
- [4] Zheng, W.; Guo, M.; Chow, T.; Bennett, D.N.; Rajagopalan, N. Sorption properties of green wastebiochar for two triazine pesticides. *J. Hazard Mater.* **2010**, *18*, 121–126.
- [5] Lehmann, J. A handful of carbon. *Nature* **2007**, *447*, 143–144.
- [6] Lehmann, J., Joseph, S. (Eds). *Biochar for Environmental Management: Science and Technology*; Earthscan: London, 2009.
- [7] Zimmerman, A.R. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environ. Sci. Technol.* **2010**, *44*, 1295–1301.
- [8] Karami, N.; Clemente, R.; Moreno-Jimenez, E.; Lepp, N.; Beesley, L. Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass (*Lolium perenne*). *J. Hazard Mater.* **2011**, *191*, 41–48.
- [9] Uchimya, M.; Lima, I.M.; Klasson, K.T.; Wartelle, L.H. Contaminant immobilization and nutrient release by biochar soil amendment: roles of natural organic matter. *Chemosphere* **2010**, *80*, 935–940.
- [10] Kookana, R.S. The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. *Aust. J. Soil. Res.* **2010**, *48*, 627–637.
- [11] *1,3-Dichloropropene: A Profile*; Dow Agro Sciences: Indianapolis, IN, 1996. Available at [http://msdssearch.dow.com/PublishedLiteratureDAS/dh\\_0932/0901b80380932f25.pdf?filepath=usag/pdfs/noreg/010-32489.pdf&fromPage=GetDoc](http://msdssearch.dow.com/PublishedLiteratureDAS/dh_0932/0901b80380932f25.pdf?filepath=usag/pdfs/noreg/010-32489.pdf&fromPage=GetDoc) (accessed May 2016).
- [12] CDPR. *Summary of Pesticide Use Report Data 2012 Indexed by Chemical*; Sacramento, CA: CDPR, 2014. Available at <http://www.cdpr.ca.gov/docs/pur/pur12rep/chmrpt12.pdf> (accessed Mar 2016).
- [13] Wang, Q.; Mao, L.; Wang, D.; Yan, D.; Ma, T.; Liu, P.; Cao, A. Emission reduction of 1, 3-dichloropropene by soil amendment with biochar. *J. Environ. Qual.* **2014**, *43*, 1656–1662.
- [14] Shen, G.; Ashworth, D.J.; Gan, J.; Yates, S.R. Biochar amendment to the soil surface reduces fumigant emissions and enhances soil micro-organism recovery. *Environ. Sci. Technol.* **2016**, *50*, 1182–1189.
- [15] Wang, Q.; Yan, D.; Liu, P.; Mao, L.; Wang, D.; Fang, W.; Li, Y.; Ouyang, C.; Guo, M.; Cao, A. Chloropicrin emission reduction by soil amendment with biochar. *Plos One* **2015**, *10*(6), e0129448.
- [16] Allaire, S.E.; Yates, S.R.; Ernst, F.F.; Gan, J. A dynamic two-dimensional system for measuring volatile organic compound volatilization and movement in soils. *J. Environ. Qual.* **2002**, *31*, 1079–1087.
- [17] Luo, L.; Ashworth, D.J.; Dungan, R.S.; Xuan, R.; Yates, S.R. Transport and fate of methyl iodide and its pest control in soils. *Environ. Sci. Technol.* **2010**, *44*, 6275–6280.
- [18] Yu, X.Y.; Ying, G.G.; Kookana, R.S. Sorption and desorption behavior of diuron in soil amended with charcoal. *J. Agric. Food Chem.* **2006**, *54*, 8545–8550.
- [19] Graber, E.R.; Tsechansky, L.; Khanukov, J.; Oka, Y. Sorption, volatilization, and efficacy of the fumigant 1, 3-dichloropropene in a biochar-amended soil. *Soil Sci. Soc. Am. J.* **2011**, *75*, 1365–1373.
- [20] Gao, F.; Yates, S.R.; Jin, Y. Laboratory study of closed an dynamic flux chambers: experimental results and implications for field application. *J. Geophys. Res.* **1998**, *103*, 26115–26125.
- [21] Vigliorchio, D.R.; Schmitt, R.V. On the methodology of nematode extraction from field samples: Baermann funnel modifications. *J. Nematology* **1993**, *15*, 438–444.
- [22] Ashworth, D.J.; Ernst, F.F.; Xuan, R.; Yates, S.R. Laboratory assessment of emission reduction strategies for the agricultural fumigants 1,3-dichloropropene and chloropicrin. *Environ. Sci. Technol.* **2009**, *43*, 5073–5078.



- [23] Ashworth, D.J.; Yates, S.R. Surface irrigation reduces the emission of volatile 1,3-dichloropropene from agricultural soils. *Environ. Sci. Technol.* **2007**, *41*, 2231–2236.
- [24] Yates, S.R.; Ashworth, D.J.; Zheng, W.; Zhang, Q.; Knuteson, J.; van Wesenbeeck, I.J. Emissions of 1,3-dichloropropene and chloropicrin after soil fumigation under field conditions. *J. Agric. Food Chem.* **2015**, *63*, 5354–5363.
- [25] Ashworth, D.J.; Yates, S.R.; van Wesenbeeck, I.J.; Stanghellini, M. Effect of co-formulation of 1,3-dichloropropene and chloropicrin on evaporative emissions from soil. *J. Agric. Food Chem.* **2015**, *63*, 415–421.
- [26] Coutinho, A.R.; Rocha, J.D.; Luengo, C.A. Preparing and characterizing biocarbon electrodes. *Fuel Process. Technol.* **2000**, *67*, 93–102.
- [27] Kolodynska, D.; Wnetrzak, R.; Leahy, J.J.; Hayes, M.H.B.; Kwapinski, W.; Hubicki, Z. Kinetic and adsorptive characterization of biochar in metal ions removal. *Chem. Eng. J.* **2012**, *197*, 295–305.
- [28] Kemper, J.M.; Ammar, E.; Mitch, W.A. Abiotic degradation of hexahydro-1,3,5-trinitro-1,3,5-triazine in the presence of hydrogen sulfide and black carbon. *Environ. Sci. Technol.* **2008**, *42*, 2118–2123.
- [29] Yates, S.R.; Ashworth, D.J.; Yates, M.D.; Luo, L. Active solarization as a nonchemical alternative to soil fumigation for controlling pests. *Soil Sci. Am. J.* **2011**, *75*, 9–16.
- [30] Park, M.K.; Kim, J.H.; Dungan, R.S. Sorption of the fumigant 1,3-dichloropropene on soil. *J. Environ. Sci. Health B* **2004**, *39*, 603–612.
- [31] *1,3-Dichloropropene Risk Characterization Document: Environmental Fate*; California Environmental Protection Agency: Sacramento, CA, 2012. Available at <http://www.cdpr.ca.gov/docs/emon/pubs/fate/memo/13-d.pdf> (accessed May 2016).
- [32] Wang, D.; Yates, S.R. Spatial and temporal distributions of 1,3-dichloropropene in soil under drip and shank application and implications for pest control efficacy using concentration-time index. *Pestic. Sci.* **1999**, *55*, 154–160.
- [33] Luo, L.; Yates, S.R.; Ashworth, S.R.; Xuan, R.; Becker, J.O. Effect of films on 1,3-dichloropropene and chloropicrin emission, soil concentration, and root-knot nematode control in a raised bed. *J. Agric. Food Chem.* **2013**, *61*, 2400–2406.
- [34] Guo, S.; Trout, T.; Qin, R. *Develop Field management Practices to Reduce Soil Fumigant Emissions*; California Department of Food and Agriculture: Sacramento, CA, 2010. Available at <https://www.cdffa.ca.gov/files/pdf/FieldMngmntPractReduceSoilFumigantEmit.pdf> (accessed Feb 2016).